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54: Title of invention - A liquid detergent composition

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Specification

1. Title of invention
A liquid detergent composition

2. Claim
(1) A liquid detergent composition consisting of the following three ingredients (a), (b) and (c);
(a) 5 - 50 weight % of surfactant
(b) 0.01 - 10 weight % of polymer latex having cationic group or tertiary amino group,
(c) 0.001 - 3 weight % of perfume.

3. Detailed explanation of the invention

[Industrial application]
The pesent invention refers to a liquid detergent composition. In other words, the present invention relates to a liquid detergent composition capable of providing a fine residual aroma to a fabric.

[Conventional technology and its problem]
The conventional method of laundering fabrics in house is usually carried out by a washer. After laundering, spinning and drying, a finishing procedure using an iron is carried out. Although the primary purpose of the lundering is to remove stains from fabrics, it is preferable that fine aroma is given to fabrics after laundering. The conventional method of providing fine aroma to fabrics has been performed by adding a high boiling point perfume which does not evaporate during drying to the detergency.
However, in case of using a large amount of laundering water (for

example, 30 liters of laundering water per one kg of laundrys), a large portion of the said perfume is washed away during laundering and rinsing. In this case, only faint aroma may be retained on the fabric.

[Method of solving the problem]

Under the said circumstance, the present inventors have made great efforts to solve the said problems. As a result, it was found that a detergent composition showing an excellent ability of retaining aroma could be obtained in case of adding polymer latex having cationic group or tertiary amino group. Thus, the present invention was accomplished by utilizing the said knowledge.

In other words, the present invention provides a liquid detergent composition consisting of the following three ingredients (a), (b) and (c);

(a) 5 - 50 weight % of surfactant

(b) 0.01 - 10 weight % of polymer latex having cationic group or tertiary amino group,

(c) 0.001 - 3 weight % of perfume.

The surfactants described in the present invention as the ingredient (a) are any conventional surfactants used in the liquid detergent compositions, and the surfactant can be used singly or as a combination of more than two compounds.

Among the said ingredient (a), anionic surfactants are linear or branched chain alkyl benzene sulfonate, alkyl or alkenyl ether sulfate, alkyl or alkenyl sulfate, olefin sulfonate, alkane sulfonate, alpha-ysulfofatty acid salt or ester, saturated or unsaturated fatty acid salts, alkyl or alkenyl ether carboxylate, amino acid type surfactants, N-acyl amino acid type surfactants, alkyl or alkenyl phosphoric acid ester or its salt, and so on.

On the other hand, amphoteric surfactants are carboxy or sulfobetaine type surfactants, etc.

Nonionic surfactants are polyoxy alkylene alkyl or alkenyl ether, polyoxyethylene alkyl phenyl ether, higher fatty acid alkanol amide or its alkylene oxide adducts, sucrose fatty acid ester, fatty acid ester, fatty acid glycerine monoester, alkyl amine oxide, etc.

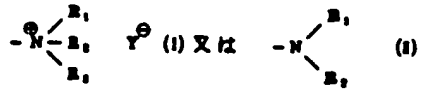
Cationic surfactants are quaternary ammonium salts, etc.

The concentration of the said ingredient (a) in a liquid detergent composition is usually 5 - 50 weight % (hereinafter, %), preferably 10 - 40 %.

In case that the concentration of the ingredient (b) is less than 5 %, a sufficient detergency becomes insufficient. On the other hand, in case that the concentration exceeds 50 %, the stability of liquid composition becomes poor.

The polymer latex compounds (Hereinafter, polymer latex containing nitrogen) having cationic group or tertiary amino group as the ingredient (b) are manufactured by a polymerization of microemulsion or

solution consisting of monomers having cationic group or tertiary amino group, or the said monomers and other water insoluble polymerizable monomers. The said microemulsion state can be created by exposing nonionic surfactant at a proper temperature which is around the phase inversion temperature or by combining anionic surfactant with proper auxiliary surfactants such as ninionic surfactants, etc. and higher alcohols, etc. The solution condition can be achieved by adding a large amount of surfactant to polymerizable monomers.
Among these methods, a preferable method is a polymerization in the microemulsion state, wherein the polymerization temoerature is set near the phase inversion temperature using nonionic surfactants and the interfacial tension between monomer and water is reduced to one dyne/cm or less, preferably 0.5 dyne / cm or less.
Monomers containing nitrogen have the following general formula (I) or (II).



(In the formula, R1, R2 and R3 are C1 - C18 alkyl group or substituting alkyl group or hydrogen atom, and these may be identical or different. Or two groups among the said three groups may form pyridyl group, heterocyclic rings such as imidazoyl group, cycloalkyl group, heterocycloalkyl group, with adjuscent nitrogen atom; Y is halogen or acid residue.). These monomers are ethylenic unsaturated monomer units containing nitrogen having cationic group or tertiary amino group.
The said ethylenic unsaturated monomer units containing nitrogen can be made into polymer latex containing nitrogen by simple industrial scale copolymerization or chemical reaction of polymers.
For examples;
monovinyl pyridines such as vinyl pyridine, 2-methyl-5-vinyl pyridine, 2-ethyl-5-vinyl pyridine, etc.; styrenes having dialkyl amino group such as N-N-dimethyl amino styrene, N,N-dimethylamino methyl styrene, etc.; esters having dialkyl amino group of acrylic acid or methacrylic acid such as N,N-dimethylamino ethyl methacrylate, N,N-dimethylamino ethyl acrylate, N,N-diethylamino ethyl methacrylate, N,N-diethylamino ethyl acrylate, N,N-dimethylamino propyl methacrylate, N,N-dimethylamino propylacrylate, N,N-diethylamino propyl methacrylate, N,N-diethylamino propyl acrylate, etc.; vinyl esters having dialkyl amino group such as 2-dimethyl amino ethyl vinyl ether, etc.; polymers obtained by the conventional copolymerization of water insoluble ethylenic unsaturated monomer and acrylic amides or methacrylamides having dialkyl amino group such as N-(N',N'-dimethylamino ethyl)methacrylamide, N-(N',N'-dimethylaminoethyl) acrylamide, N-(N',N'-diethylaminoethyl) methacrylamide, N-(N',N'-diethylaminoethyl)

acrylamide, N-(N',N'-dimethylaminopropyl) methacrylamide, N-(N',N'-dimethylaminopropyl) acrylamide, N-(N',N'-diethylaminopropyl) methacryl amide, N-(N'N'-diethylaminopropyl) acrylamide, etc.. Furthermore, these are polymers subjected for a quaternarization using the conventional quaternarizing agents such as halogenated alkyl (C1-C18 alkyl group; chlorine, bromine, Iodine as the halogen), halogenated benzyl such as benzyl chloride, benzyl bromide, etc.; methane sulfonic acid, alkyl esters (C1 - C18 alkyl group) of alkyl or aryl sulfonic acid such as benzene sulfonic acid or toluene sulfonic acid, and dialkyl sulfuric acid, and so on.

(b) Copolymers between water insoluble ethylenic unsaturated monomers and ethylenic unsaturated monomers having halogenated methyl group (-CH2X) such as chlormethylstyrene, 3-chloro-1-propene, 3-bromo-1-ane, propene, 3-bromo-1-propene, 2-chlorethylacrylate, 2-chlorethyl methacrylate, 2-bromoethyl acrylate, 2-bromoethyl methacrylate, 3-kmethylochloropropylacrylate, 3-chloropropyl acrylate, 3-chloropropyl methacrylate, 3-bromopropyl acrylate, 3-bromopropyl methacrylate, 4-chloropropylacrylate, 4-chloropropyl methacrylate, 2-chloroethylvinyl ether, etc.; or reaction products between polymers having halogenated methyl group such as chlormethylated polymers of copolymer between polystyrene or styrene and other water insoluble ethylenic unsaturated monomers, and aromatic amines such as aliphatic tertiary amine or dimethylaniline, diethylaniline, tribenzyl aniline such as trimethylamine, triethylamine, tripropylamine, tributylamine, triamylamine, n-octyldimethylamine, n-dodecyldimethylamine, n-tetradecyl dimethyl amine, etc.

(c) The epoxy group is opened by allowing secondary amine to react with polymer obtained by copolymerization between water insoluble ethylenic unsaturated monomer and ethylenic unsaturated monomer having epoxy group such as (meta)acrylic acid glycidyl, vinylphenyl glycidyl ether, vinylphenyl ethylene oxide, allylglycidyl ether, etc. and at the same time, tertiary amino group is introduced, and then the compound is quaternarized by the method described in (a).

(d) Reaction product between cationizing agent such as glycidyl trimethyl ammonium hydrochloride or 3-chloro-2-hydroxypropyl trimethyl ammonium salt and copolymer between ethylenic unsaturated monomer having hydroxy group and water insouble ethylenic unsaturated monomer such as 2-hydroxy ethyl acrylate, 2-hydroxy ethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, N-2-hydroxyethyl acrylamide, etc.; or polymer having hydroxy group such as saponified copolymer between water insoluble ethylenic unsaturated monomer and fatty acid ester of vinyl alcohol.

(e) Copolymer between water insoluble ethylenic unsaturated monomer and ethylenic unsaturated monomer having cationic group which is obtained by quaternirization of ethylenic unsaturated monomer having tertiary amino group described in (a) using quaternizing agent described in (b) or by the reaction between ethylenic unsaturated

monomer having chloromethyl group described in (b) and aliphatic tertiary amine and aromatic amine.
These compounds listed in (a) - (e) are not necessarily quaternirized or salt form, and may be tertiery salts having the general formula (II). The said tertiary amino group shows weak cationic activity in an aqueous system (neutaral to acidic solution).
Water insoluble polymerizable monomers used for preparing polymers described in (a) - (e) may be any conventional monomers used in the emulsion polymerization. For examples, these monomers are ethylenic unsaturated monomers such as ethylene, propylene, isobuten, buten-1, etc.; aromatic vinyl monomers such as styrene, alpha-methyl styrene, vinyl toluene, halogenated styrene, divinyl benzene, etc.; C1 - C20 acrylic acid esters such as acrylic acid ethyl, acrylic acid butyl, acrylic acid 2-ethylhexyl, etc.; C1 - C20 methacrylic acid esters such as methacrylic acid ethyl, methacrylic acid butyl, methacrylic acid lauryl, etc.; vinyl esters such as vinyl acetate, vinyl propionate, etc.; C1 - C20 vinyl ethers such as ethyl vinyl ether, butyl vinyl ether, etc.; C1 - C20 vinyl ketones such as methyl vinyl ketone, ethyl vinyl ketone, etc.; vinyl cyane monomers such as acrylonitrile, methacrylonitrile, etc.; halogenated vinyl such as vinyl chloride, vinyl bromide, vinylidene chloride, vinylidene bromide, etc.; and aliphatic covalent dienes such as halogenated vinylidene, 1,3-butadiene, 2-methyl-1,3-butadiene, etc.; and so on.
These monomers can be used singly or a mixture of more than two compounds. Among these monomers, preferable monomers are alpha-, beta- unsaturated carboxylic acid ester type monomers such as acrylate, methacrylate, etc. Furthermore, copolymers may be prepared by allowing maleic anhydride or water soluble monomers, stylene sulfonic acid, or stylene sulfonate, vinyl naphthalene sulfonic acid (sulfonate), acrylic acid (acrylate) to react with the said monomers.
In case of preparing polymer latex containing nitrogen described in the present invention, the concentration of monomer containing nitrogen to water insoluble polymerizable monomer may be 0.05 - 55 %.
A preferable method of manufacturing the polymer latex containing nitrogen described in the present invention is as follows: In other words, an aqueous solution is prepared by adding surfactant to a reaction vessel containing water, and the surfactant solution is heated at the phase converison temperature, where the phase of surfactant micelle is converted. The polymerization is initiated by adding polymerizable monomer and radical polymerization initiator if necessary while the interfacial tension between the monomer and water is maintained less than one dyne/cm, preferably 0 - 0.5 dyne/cm. The polymerization is carried out by adding polymerizable monomer gradually wherein the interfacial tension between the surfactant solution and the monomer phase is maintained within the specified range.
Radical polymerization intiators described in the present invention are persulates such as potassium persulfate, sodium persulfate,

ammonium persulfate, etc. ; azo compounds such as 2,2'-azobis(2-amidino propane) mineral acid salts, azobis cyanobutadienic acid (illegible) and its alkali metal salt and ammonium salt, 1,1'-azobis cyclohexane carbonitrile, etc.; Redox type initiators such as tartaric acid - hydrogen peroxide, Rongalit - peroxide, ascorbic acid - peroxide, etc.; and so on.

In case that cationic surfactant is used as the polymer system, 2,2'-azobis (2-amidinopropane) mineral oil acid is preferable. In case that other polymer systems are used, persulfates are preferable.

The amount of the radical polymerization initiator in 100 weight parts of monomer may be 1 - 5 weight parts, preferably 0.1 - 3 weight parts.

In the said method, the reaction temperature is the maximum temperature in the solubilization range near the phase conversion temperature, and may be 50 - 90° C, preferably. Furthermore, a time required for the polymerization is significantly affected by type of monomer, composition of monomer, concentration of monomer, concentration of radical polymerization initiator, polymerization temperature, etc. and may be usually 5 - 50 hours.

Polymer latex containing nitrogen may be the polymers having cationic group or tertiary amino group in the molecule. However, the said polymers can be prepared by activating non-cationic polymer latex with polymer having cationic group or tertiary amino group as the protective colloid agent.

As the said polymer latex containing nitrogen contains usually more than 200 - 300 ppm of residual monomers, it is preferable to remove the said residual monomers before the polymer latex is used in a liquid detergent composition described in the present invention. Methods of removing the said residual monomers may be a distillation method under reduced pressure, steam distillation under reduced pressure, thin membrane separation under reduced pressure, bubbling by introducing air, adsorption using adsorbent, and so on.

On the other hand, an average particle size of the polymer latex containing nitrogen is 0.005 - 0.2 um, and it is preferable that more than 95 % of the paricles should be in the said range.

A liquid detergent for fabric described in the present invention is prepared as follows: in other words, the ingredient (b) prepared by the method described above is directly added to a liquid detergent base composition or after the ingredient (b) is concentrated to a specified level, the concentrated liquid (suspension) may be added to the base composition. The concentration of the ingredient (b) in the liquid detergent composition may be 0.01 - 10 %, preferably 0.05 - 5 %, in the residue of the composition after water is removed.

Perfumes as the ingredient (c) are any conventional perfumes having the basic structure of alcohol, ketone, ether, lactone, ester, etc. For example, these are 2,6-dinitro-3,5-dimethyl-4-acetyl-tert-butyl

benzene, 7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydro naphthalene, synthetic santalic acid (?), patchouli alcohol, methylcedriron, 1,2-benzopyran, 4-(2,6,6-trimethyl-2-cyclohexene-1-il)-3-butene-2-on, benzyl salicylate, alpha-n-hexyl cinnamic aldehyde, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxyaldehyde, 3,7-dimethyl-6-octene-1-ol, beta-phenylethylalcohol, 1-methyl-4-isopropyl-1-cyclohexene-8-ol, 3,7-dimethyl-1,6-octadiene-3-ol, 3,7-dimethyloctanol-3, gamma-undecalactone, 3,4-methyl-enedioxy benzaldehyde, vetivelol, amy salicylate, beta-naphthol methyl ether, 2-trans-3,7-dimethyl-2,6-octadiene-1-ol, 3,7-dimethyl-1,6-octadiene-3-il acetate, p-menthe-1-en-8-il acetate, 1-methyl-p-isopropenyl-1-cyclohexene, 2-methyl-6-methylene-7-octane-2-ol, 3,7-dimethyl-2,6-octadiene-8-il nitrile, 5-(2-methylene-6,6-dimethyl cyclohexyl)-4-pentene-3-on, p-tert-butyl cyclohexyl acetate, 2-methoxy-4-allyl phenol, 3-hydroxy2-methyl-4-pyron, p-tert-butyl-alpha-methylhydroxy cinnamic aldehyde, and so on. The concentration of the said ingredient (c) in the liquid detergent cmposition may be 0.01 - 10 %, preferably 0.05 - 5 %.

Although the liquid detergent composition described in the present invention consists of the said three ingredients (a), (b) and (c), other ingredients can be added if necessary.

Other ingredients are lower alcohols such as ethanol, etc., lower alkyl benzene sulfonates such as benzene sulfonate, p-toluene sulfonate, etc.; glycols such as propyleneglycol, etc.; acetyl- benzene sulfonates, acetamides, pyridine dicarboxylic acid amides, benzoates or urea and other solubilizers; polymer electrolytes such as polyacrylic acid, polyaconitic acid, etc.; non-dissociating polymers such as polyvinylalcohol, polyvinylpyrrolidone, etc.; divalent metal ion chelating agents such as organic acids salts of oxycarboxylates and diglycolic acid, etc.; inorganic electrolytes such as sulfate, etc.; anti-redeposition agents such as polyethylene glycol, carboxy methyl cellulose, etc.; enzymes such as protease, amylase, lipase, cellulase, etc.; enzyme stabilizers such as calcium chloride, etc.; antioxidants such as tertial butyl hydroxy toluene, distyrenated cresol, etc.; fluorescent dye, blue tinting agent, and so on. In other words, any conventional ingredients can be used according to the purpose of the use.

[Effect of the invention]

The liquid detergent composition described in the present invention is able to provide a fine aroma to fabrics even if the fabrics are washed and rinsed with a large amount of water in spite of the fact that only small amount of perfume is added to the composition.

[Practical example]

The present invention shall be explained in details in the following reference examples and practical examples.

Reference example 1:

(i) A 343 g of water, 21 g of polyoxyethylene (35) nonylphenyl ether and a 8 g of water containing 0.8 g of 2,2'-azobis(2-amidinopropane) hydrochloride were placed in a separatory flask having a stirrer, and the air in the flask was replaced with nitrogen gas. The flask was then heated at 62° C with a constant stirring while nitrogen gas was introduced into the reaction system, and 97 g of n-butylacrylate and 3 g of N,N'-dimethylaminoethylacrylate were added dropwisely in approximately 2 hours, and the polymerization was carried out for another 7 hours. After completing the polymerization, the reaction system was allowed to cool, and then, the reaction mixture was filtered through a 200 mesh meal net. Thus, latex A (n-butylacrylate / dimethylamino ethyl acrylate = 97 / 3, 300 ppm of residual monomer) was obtained.

(ii) The latex obtained in (i) was subjected for a steam distillation at 90° C for 4 hours, and purified latex A containing 40 ppm of residual monomer (average particle size based on te weight : 0.07 microns; 100 % of the particles was within the range of 0.005 - 0.2 microns) was obtained.

Practical example 1:

A liquid detergent composition containing the following ingredients was prepared using the purified latex A prepared in the reference example 1. The function of the liquid detergent composition (aroma retaining ability) was tested. The result is shown in Table 1.

(Ingredients)

poly(10)oxyethylene alkyl(C12-13) ether	15 (%)
coconut fatty acid monoethanol amide	3
purified latex A	0 or 1
perfume *	Table 1
ethanol	5
water	Balance

* The composition of the perfume is shown in the following.

2,6-dinitro-3,5-dimethyl-4-acetyl-tert-butylbenzene	8 (%)
gamma-undecalactone	1
patchouli alcohol	3
1,2-bwnzopyrane	7
3,4-methyl-enedioxy benzaldehyde	5
vetivelol	1
amy salicylate	8
synthetic sandol	5
beta-phenyl ethayl alcohol	20
beta-naphthol methyl ether	5

2-trans-3,7-dimethyl-2,6-octadiene-1-ol	10
3,7-dimethyl-1,6-octadiene-3-il acetate	6
3,7-dimethyl-1,6-octadiene-3-ol	14
p-menth-1-ene-8-il acetate	10
Total	100 %

(Test method)

(1) Laundering method

Cotton broad clothes (30 x 30 cm) were placed in a small size washer (Model NA-35 , manufacutured by Matsushita Denki Sangyo K.K.) and 3 liters of 0.25 % of detergent solution was loaded and the laundering was carried out for 10 min. Rinse step was carried out as follows: after discharging all laundering water, 3 liters of tap water was added to the washer and rinse was carried out for 2 min, and the said step was repeated twice. The test cloth was then span for 30 sec in the washer and was allowed to stand at 20° C and 65% RH for 24 hours.

(2) Evaluation of aroma:

Three examiners (18 years old female (A), 25 years old female (B), and 31 years old male (C)) evaluated the degree of aroma, and the evaluation of aroma was carried out by calculating an average score of three examiners (The strongest aroma : 1 point, the weakest aroma : 5 points).

Table 1:

表 1

a (%)	b (%)	c	d	e	f
精製カチオンラテックスA	香料	パネラーA	パネラーB	パネラーC	平均点
0	0.3	4	3	4	3.7
1	0.3	1	1	1	1
1	0.1	2	2	2	2
1	0.05	3	4	3	3.3

a: purified cation latex A (%), b: perfume (%), c: examiner A, d: examiner (B), e: examiner (C), f: average score.

Reference example 2:

Latex B (n-butyl acrylate / dimethyl amino ethyl acrylate = 70 / 30; 35 ppm of residual monomer) and purified latex B (average particle size based on the weight : 0.10 microns; and 96 % of particles was in the range of 0.005 - 0.2 microns) were prepared in the same manner as described in the reference example 1 (i) and

(ii) and the evaluation of aroma was carried out in the same manner as described above.
The result is shown in Table 2.

(Ingredients)

poly(10)oxyethylene alkyl(C12-13) ether	15 (%)
coconut fatty acid monoethanol amide	3
purified latex B	0 or 1.5
perfume *	Table 2
ethanol	5
water	balance

* The composition of the perfume is shown in the following.

1-methyl-p-isopropenyl-1-cyclohexene	15 (%)
2-methyl-6-methylene-7-octane-2-ol	3
3,7-dimethyl-2,6-octadiene-8-il nitrile	1
3,7-dimethyl-1,6-octadiene-3-ol	12
2-trans-3,7-dimethyl-2,6-octadiene-1-ol	12.5
1-methyl-4-isopropyl-1-cyclohexene-8-ol	5
beta-phenyl ethyl alcohol	20
5-(2-methylene-6,6-dimethylcyclohexyl)-4-pentene-3-one	10
p-tert-butylcyclohexyl acetate	10
2-methoxy-4-allylphenol	5
3-hydroxy-2-methyl-4-pyron	0.5
p-tert-butyl-alpha-methylhydrocinnamic aldehyde	3
3,7-dimethyl-1,6-octadiene-3-il acetate	3
Total	100 %

Table 2:

表 2	b	c	d	e	f
精製カチオンラテックスB (%) a	香料 (%)	パネラーA	パネラーB	パネラーC	平均点
0	0.3	4	4	4	4
1.5	0.3	1	1	1	1
1.5	0.2	2	2	2	2
1.5	0.1	3	3	3	3

a: purified cation latex B (%), b: perfume (%), c: examiner (A), d: examiner (B), e: examiner (C), d: average score